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# Structure factor of simple liquid metals using hard sphere Yukawa reference system

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**Abstract:** The structure factors of simple liquid metals are calculated using a hard sphere Yukawa reference system together with the Cummings' potential in Random Phase approximation. The results are in good agreement with experiments particularly upto the first peak, for the liquid alkali metals, showing better agreement overall.

**Keywords:** Hard sphere Yukawa reference system, direct correlation function.

**PACS No:** 61.25 (Liquid metals)

## 1. Introduction

The calculation of the structure factors $S(q)$ of the liquid metals from model pair potential has proceeded by using perturbation methods. These methods involved the division of the potential into a core which is normally repulsive and a perturbation contribution. In many cases, the core has been hard sphere as the exact Percus-Yevick (PY) solution is available. If one uses this solution for the liquid metals their density range is normally such that PY solution has to be corrected slightly by use of, say, Verlet-Weiss (1972) parametrization. This procedure was introduced to achieve better agreement with the simulation results for hard spheres. A more recent approach to improve this agreement has been by Waisman (1973) with the inclusion of an attractive Yukawa tail, i.e., a hard-sphere-Yukawa (HSY). The advantage of this method over the VW approach is that the direct correlation function (DCF) is evaluated and this can be directly related to the structure factor. A number of authors (Li *et al* 1986, Hausleitner and Hafner 1988) have recently applied the Waisman approach to liquid metals using a repulsive Yukawa tail. This results in a softer core and also a lower variational upper bound to the free energy than the hard sphere reference system.

An attempt has been made, when describing the liquid metals, to soften the hard sphere core by using the WCA method (Kumaravadivel and Evans 1976). Although this method, together with VW correction, has been successful for some of the harder core such as Pb, Al, Mg, for the alkali metals the results were not as good. In the present paper, we calculate the structure factor for a number of

the simple liquid metals using the hard sphere-Yukawa reference system solved by Waisman (1973). The determination of the relevant parameters for the Waisman solution involves the solution of a complex set of equations. We follow an alternative simple procedure proposed by Henderson and Blum (1976). These authors have adjusted the Yukawa tail of the HSY potential to give the known pressure and compressibility of a fluid of hard spheres. The solution is used to obtain a generalized mean spherical approximation (GMSA) for the direct correlation function. This solution is then simplified and this simplification is used below to describe our hard sphere reference system (HSY). For perturbation part, we use the Cummings' potential (Bretonnet 1983) in the random phase approximation (RPA).

## 2. The direct correlation function

Waisman (1973) was able to solve the problem

$$c(x)=kx^{-1}\exp[-z(x-1)] \qquad x>1 \tag{1a}$$

$$g(x)=0 \qquad x<1 \tag{1b}$$

where $x=r/\sigma$ and $\sigma$ is the hard core diameter. The Ornstein-Zernike equation relates the radial distribution function $g(x)$ and the direct correlation function (dcf) $c(x)$. The Waisman solution for dcf was

$$-c(x)=a+bx+\eta a\frac{x^3}{2}+V[1-\exp(-zx)]/(zx) + V^2[\cosh zx-1)/(2kz^2\exp(z)] \qquad x<1 \tag{2}$$

where $\eta$ is the packing fraction and $a$, $b$, $k$, $z$ and $V$ are parameters determined from a complex set of equations. Henderson and Blum (1976) have simplified the GMSA by finding approximations to the parameters valid for higher packing fractions, such as for liquids. The Henderson and Blum expressions are

$$a=a_0+ka_1\ ;\ b=b_0+kb_1\ ;\ V=kV_1 \tag{3}$$

where $a$, $b$ and $V$ are the packing fraction dependent parameters and expressions for $a$, $b$ and $V$ are given elsewhere (HB 1976).

The Random Phase approximation allows us to write the expression for $c(q)$ of the system in terms of the reference system and its perturbation $\phi_1(q)$ as

$$c(q)=c_{HSY}(q)-\beta\phi_1(q) \tag{4}$$

where $c_{HSY}(q)$ is the Fourier transform of eqn. (2) and the expression of $c_{HSY}(q)$ is written in the paper of Hausleitner and Hafner (1988). The perturbation $\beta\phi_1(q)$ is the Fourier transform of the Cummings potential (see Khanna and McLaughin 1989). The structure factor can now be calculated using the expression

$$S(q)=\frac{1}{(1-c(q))} \tag{5}$$

## 3. Numerical results

In this section the structure factors of the simple liquid metals calculated from the HSY $c(q)$ using eqn. (4), are compared with the experimental results given

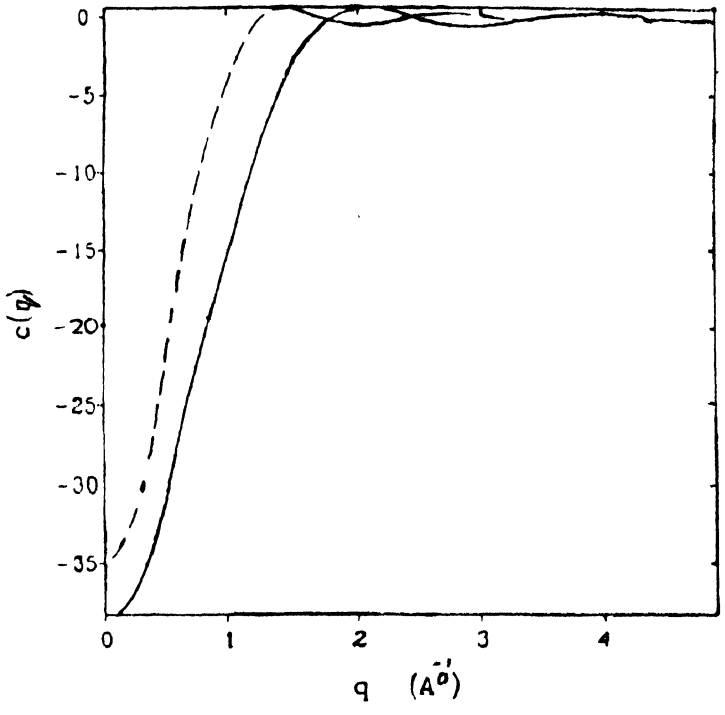


**Figure 1.** The direct correlation function $c(q)$ for $\eta = 0.45$. HS (——), HSY (- - -).

by Waseda (1980). The hard sphere Yukawa reference system parameter $a$, $b$, $k$ and $z$ are dependent on the packing fraction $\eta$ of the system or for a given density,

**Table 1.** Values of the parameters $K$, $Z$, $A$, $B$ and $v$ for HSY used in the calculations.

| Metal | $\eta$ | $K$ | $Z$ | $A$ | $B$ | $v$ | $\rho$ (au)$^{-1}$ |
|---|---|---|---|---|---|---|---|
| Na | .464 | 1.0179 | 33.162 | 40.756 | −46.242 | 1.466 | .0036 |
| K | .460 | 0.9796 | 32.542 | 39.302 | −44.431 | 1.402 | .00188 |
| Rb | .468 | 1.057 | 33.796 | 42.272 | −48.133 | 1.533 | .001539 |
| Al | .480 | 1.1865 | 35.787 | 47.2168 | −54.3304 | 1.7515 | .00785 |
| Mg | .4525 | 0.9116 | 31.415 | 36.730 | −41.2373 | 1.2892 | .00567 |
| | | | Comparison of Reference System Parameters | | | | |
| Waisman | 0.49 | 1.336 | 28.751 | 51.85 | −60.278 | 2.432 | |
| HB | 0.49 | 1.306 | 37.554 | 51.85 | −60.162 | 1.957 | |

dependent on hard sphere diameter. This free parameter $\eta$ is used to adjust the position and height of the first peak. The parametric values obtained using HB approximation are compared with the single numerical results available of Waisman (1973) i.e. $\eta=0.49$ in Table 1. We find that there is not a significant

**Table 2.** Cummings potential parameters.

| Metal | $T$ (K) | $\eta$ | $\sigma$ (au) | $x_1$ | $x_2$ | $a_1$ | $a_2$ |
|---|---|---|---|---|---|---|---|
| Na | 378 | 0.464 | 6.27 | −0.275 | 0.420 | 2.155 | 6.06 |
| K | 343 | 0.460 | 7.76 | −0.539 | 0.647 | 3.176 | 6.015 |
| Rb | 313 | 0.468 | 8.34 | −0.539 | 0.684 | 3.00 | 6.06 |
| Al | 943 | 0.480 | 4.89 | −0.851 | 0.255 | 17.256 | 9.452 |
| Mg | 953 | 0.4525 | 5.34 | −1.1 | 1.835 | 17.256 | 10.003 |

difference between the exact Waisman solution and HB approximation. We also compare our results with hard sphere reference system by drawing dcf of HS and HSY system in Figure 1. These two HSY and HS reference systems considerably differ from each other. The values used for the parameters in the

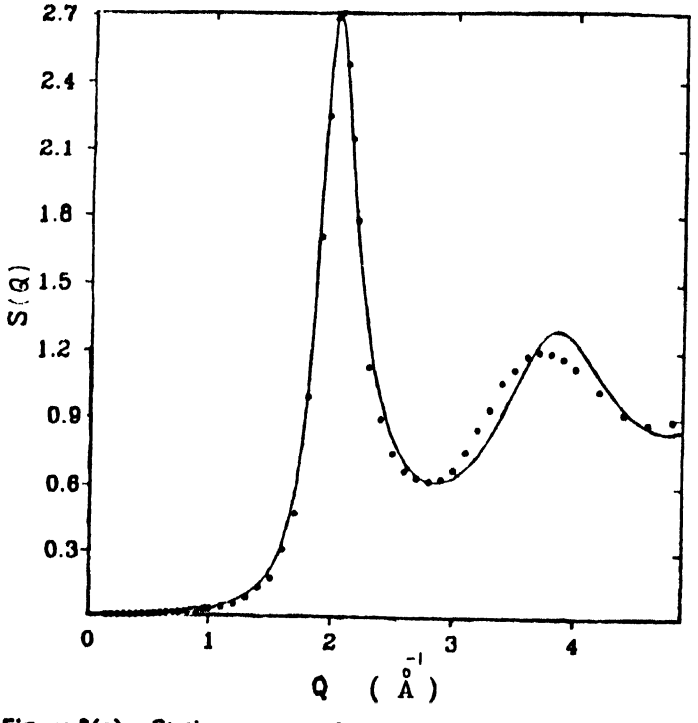


**Figure 2(a).** Static structure factors for Na by using eqn. 4 in units of $q=Q\sigma$ Full circles are experimental results (Waseda 1980).

reference system and Cumming's potential for the alkali metals Na, K, Rb and for the harder core metals Al and Mg are given in Tables 1 and 2. The calculations

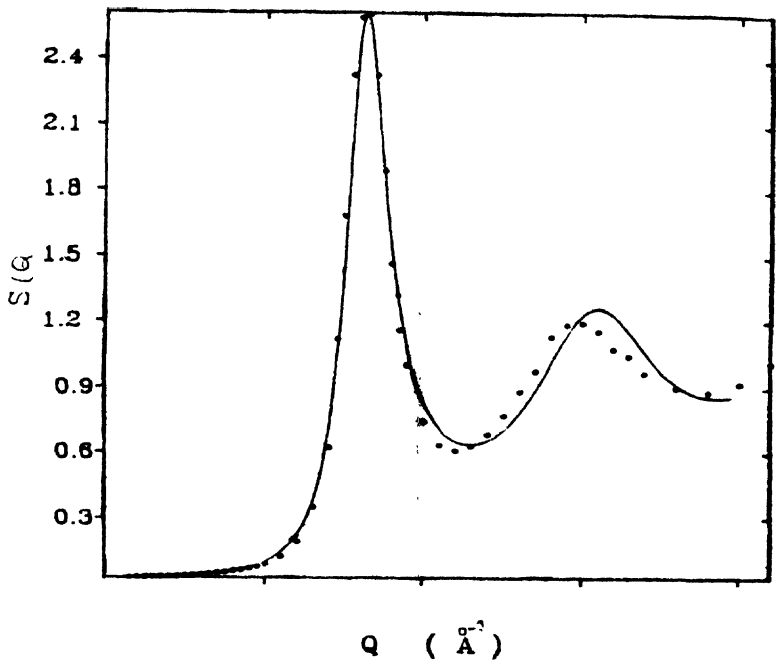


**Figure 2(b).** Static struture factors for K by using eqn. 4 in units of $q = Q r_s$. Full circles are experimental results (Waseda 1980).

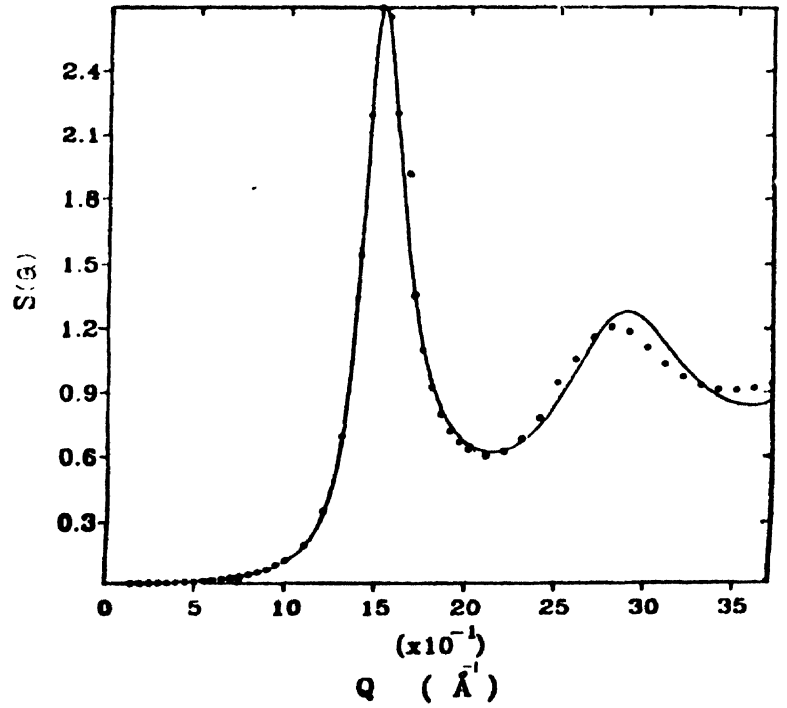


**Figure 2(c).** Static structure factors for Rb by using eqn. 4 in units of $q = Q\sigma$ Full circles are experimental results (Waseda 1980).

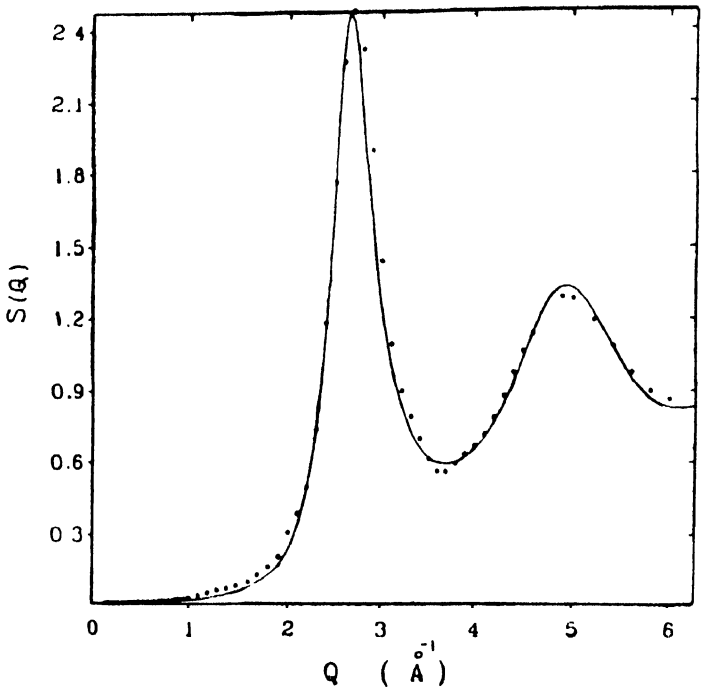


**Figure 2(d).** Static structure factors for Al by using eqn. 4 rn units of $q = Q\sigma$. Full circles are experimental resdlts (Waseda 1980).

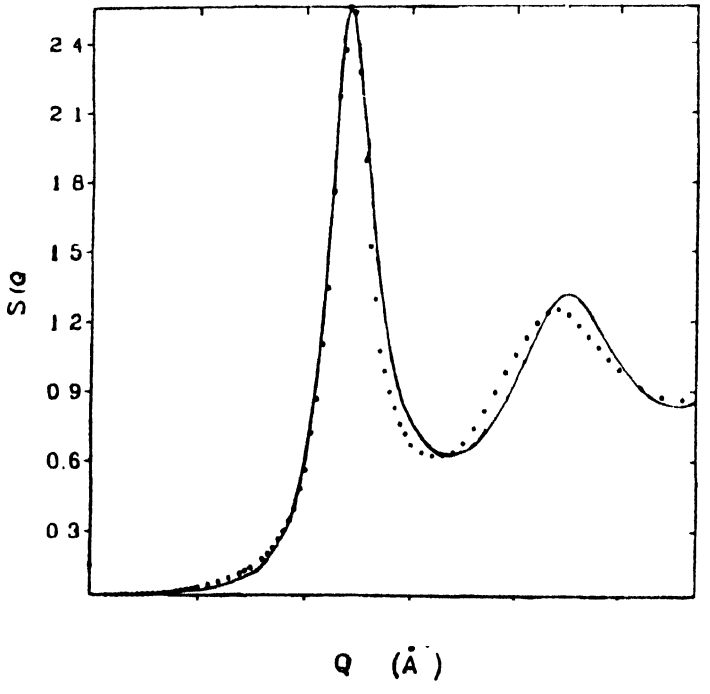


**Figure 2(e).** Static structure factors for Mg by using eqn. (4) in units of $q = Q\sigma$. Full circles are experimental results (Waseda 1980).

of low angle structure factors and long wavelength limit are discussed by one of the present authors in earlier work (McLaughlin and Khanna 1990). These calculations have illustrated the importance of the long range Friedel oscillations, employed through Cummings' potential in HSY system. Here, we present the full structure factors of simple metals using HSY reference system and Cummings' potential in Figures 2(a-e).

For the alkali metals excellent agreement with exper ment is achieved at low $Q$ and the first peak. Beyond the first peak the structure factor shows a small phase shift. This is a feature of all the hard sphere approaches even when softening of a potential is incorporated by WCA (McLaughlin and Young 1982). Even the Waisman approach using a repulsive Yukawa tail to soften the core shows the same characteristic (Hausleitner and Hafner 1988). The agreement beyond first peak becomes poorer as we move from alkali metals (soft pair potential) to Al and Mg (steeper potentials). On the contrary, the softness of the potential of the alkali metals has been a difficulty for the approaches that soften the hard sphere system such as the WCA (McLaughlin 1982) but for the steeper potential such as Mg or Pb good agreement has been achieved, atleast for high $Q$. It is well known that soft potentials the WCA-Blip function leads to a spurious peak at $q \simeq \pi/\sigma$ in $S(q)$, because $B\sigma(q)$ has its maximum there (Khal and Hafner 1985). In HSY approach we do not find such spurious peak.

## 4. Conclusion

The HSY form has been used to improve the hard sphere solution of Percus and Yevick while the Cummings' potential has provided softness and the longer range oscillations in the potential. Softness in core as well as in tail, as recently commented by Arlinghaus and Cummings' (1987) resulted in good agreement with experimental results for the alkalis particularly in low $Q$ range. As expected for the liquid metals with the steeper potential such as Mg the agreement is not as good.

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